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Research Article

Synthesis of Binaphthyl-Based Push-Pull Chromophores with Supramolecularly Polarizable Acceptor Ends

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We report on the design and synthesis of new enantiopure binaphthyl derivatives in which electron-donating and electron-withdrawing substituents are placed in direct conjugation, to create push-pull dyes potentially active for NLO applications. The dyes, unprecedentedly, extend their π-bridge from the 3,3′ positions of the binaphthyl units and incorporate as acceptors 1,3-dicarbonyl and tetrafluorobenzene units, useful for further supramolecular polarization of the chiral dyes.

1. Introduction

Conjugated organic compounds and polymers are employed in many technological applications and widely studied either in solution or in bulk [1]. Second harmonic generation (SHG), a nonlinear optical property which is at the foundation for advanced technologies in materials science and biological imaging, requires a fully conjugated organic structure at the molecular level and the absence of a center of symmetry in the bulk [2–6]. Centrosymmetrical molecules need stringent conditions in the self-assembly process in order to generate efficient materials for SHG [7, 8]. On the other hand, molecular chirality offers simple design principles for push-pull and noncentrosymmetric molecules, and the nanostructuring via self-assembly of chiral organic dyes has been shown to have pronounced effects and amplifications of their SHG response [9]. Binaphthyl compounds have been exploited for the realization of second-order nonlinear optical (NLO) materials, having the combined advantages of being chromophores and carrying the required element of chirality for bulk anisotropy [10–17]. In fact, binaphthyl systems, such as that shown in Figure 1, are composed of two chromophores joined through an aryl-aryl bond, which is the element (axis) of chirality, with dihedral angles usually close to 90°, so that interchromophoric conjugation is not efficient. The application of the binaphthyl compounds in the field of nanosciences is recent and not yet fully explored [18–29]. In all previously reported examples of binaphthyl dyes for NLO applications, the molecular design expressing the push-pull concept was developed by placing electron donating groups in the 2,2′ positions and the electron accepting units in the 6,6′ positions (Figure 1) [10–17].

Our research group studied various compounds in which an electron donating group is conjugated through a π-bridge to an electron accepting group which is a 1,3-dicarbonyl unit able to undergo further polarization by coordination with Lewis-like metal ions [30–35]. Examples of chromophores able to undergo polarization and head to tail orientation upon the use of specific supramolecular interactions are known [36–38]. In this work, we present our synthetic approach for the obtainment of enantiopure binaphthyl systems of novel design and conception, in which the π-bridge is extended through the 3,3′ position. The electron deficient moieties, in the form of 1,3-dicarbonyl units for compounds **1** and iodotetrafluorobenzene units for compounds **2**, can be in principle further polarized by means of complexation with metal cations in the former case or halogen bonding acceptors (e.g., pyridines) in the latter case (Figure 2).

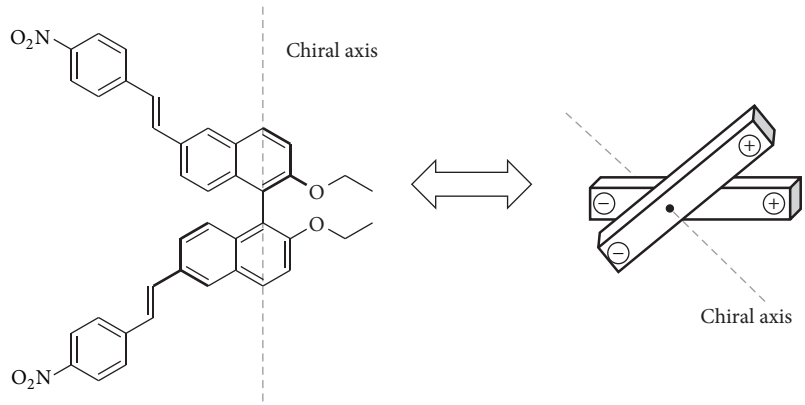


Figure 1: The molecular design for push-pull chiral binaphthyl derivatives [16].

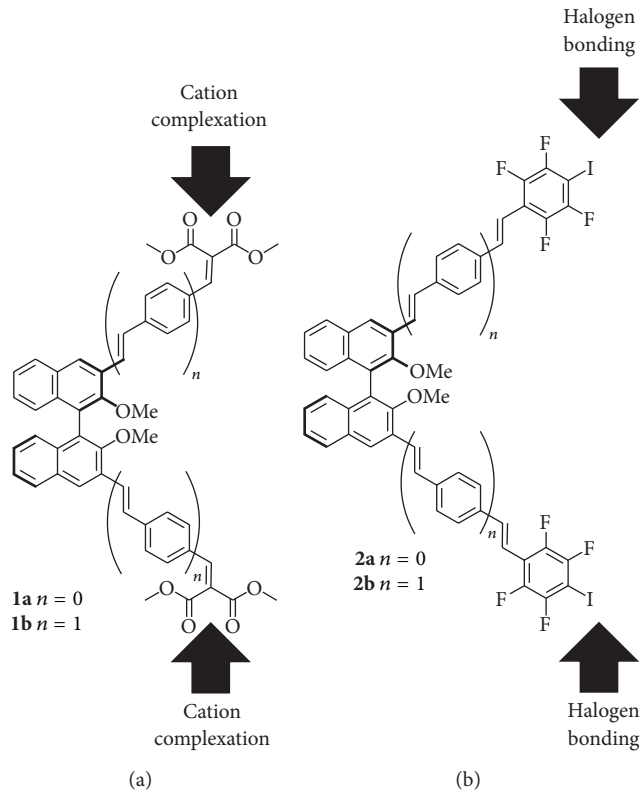
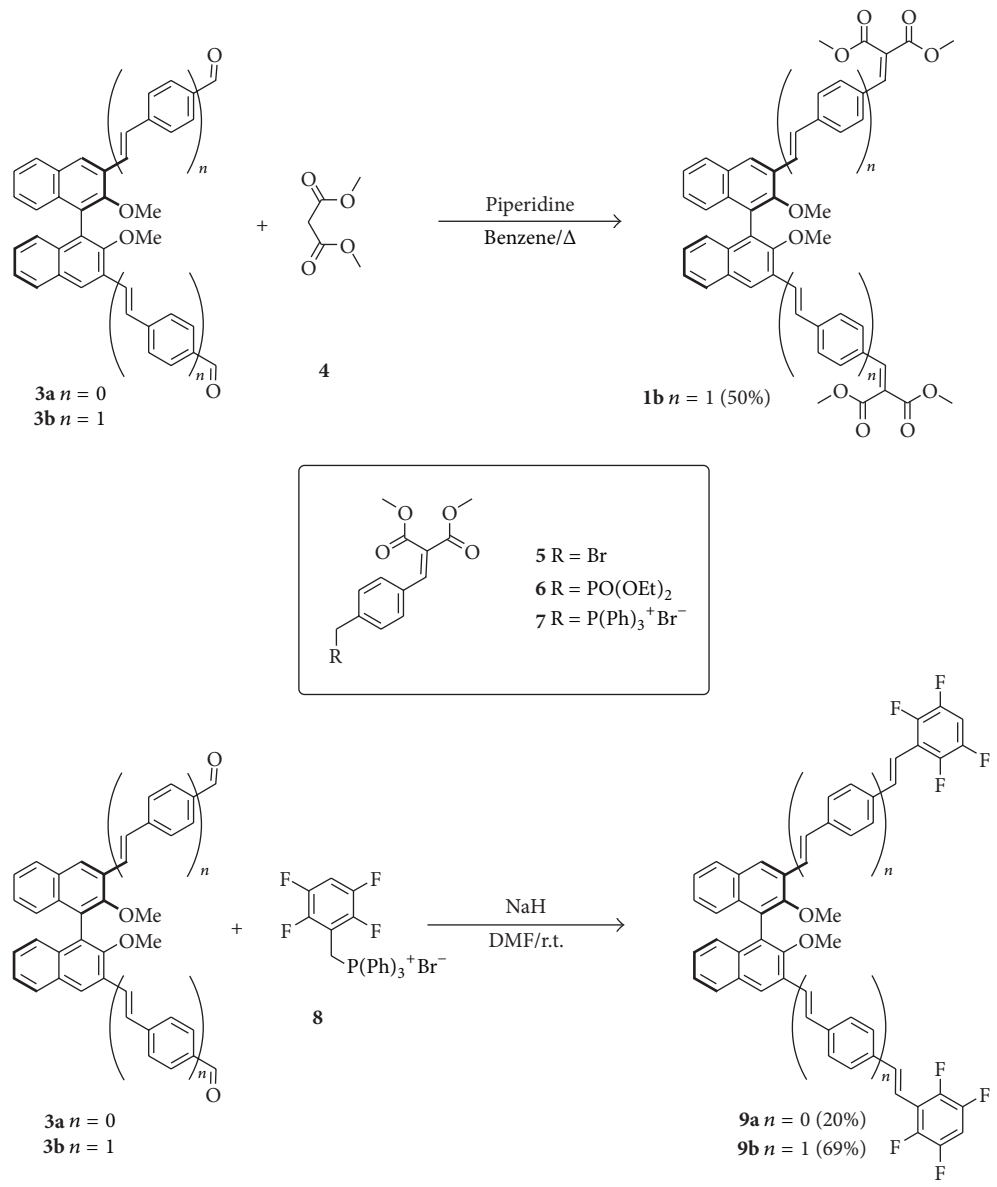


Figure 2: Target compounds subject of this paper.

2. Results and Discussion

2.1. Synthesis of the Molecular Modules. In our design strategy, the electron-donating alkoxy substituents in the 2,2′ positions are in an *ortho* relationship with respect to the growing π-bridge in the 3,3′ position, achieving efficient conjugation with the π-bridge. The synthesis of the key compounds is shown in Scheme 1. Enantiopure starting materials for this work were obtained via multistep syntheses starting from the commercially available enantiopure (*R*)-BINOL, which was chemically transformed under nonracemizing conditions.

Compound (*R*)-**1b** (Scheme 1, top) was synthesized using a Knoevenagel condensation reaction between elongated, recently reported dialdehyde (*R*)-**3b** [39] and dimethyl malonate **4**. The reaction was carried out under classical conditions (piperidine as the catalyst, continuous H_2O removal with a Dean-Stark apparatus); the compound was isolated in good yield after column chromatography and fully characterized (see Appendix). On the contrary, using identical conditions, compound (*R*)-**1a** could not be obtained from dialdehyde (*R*)-**3a**. It is likely that the enhanced steric hindrance caused by the presence of the methoxy group *ortho* to the aldehyde functionality is responsible for the



Scheme 1: Synthesis of the molecular modules described in this paper.

reduced reactivity in this case. We also explored alternative reaction approaches to the synthesis of (*R*)-**1b** by means of olefination reaction (Wittig, or Horner-Wadsworth-Emmons methodologies) involving binaphthyl dialdehyde derivative (*R*)-**3a** in combination with π-extended phosphonate **6** or phosphonium salt **7**. In both cases, however, decomposition of **6** or **7** occurred in the presence of the strong bases required for Wittig or HWE reactions, presumably because a carbon-carbon double bond, which is highly activated towards nucleophilic attack, is present in the π-extended structures.

Reaction of (*R*)-**3a** and (*R*)-**3b** with phosphonium salt **8** using standard Wittig conditions (NaH, DMF) afforded compounds (*R*)-**9a** and (*R*)-**9b** in acceptable yields. The stereochemistry of the newly carbon-carbon double bond was determined to be stereopure *trans* by NMR spectroscopy.

With the aim to expand the supramolecular functionalities of **9b** we targeted the formation of halogen bonding donor sites by adding an iodine atom for each tetrafluorophenyl ring. It is known that iodine atoms, when they are covalently bound to strong electron-withdrawing groups, such as fluorinated residues, function as very efficient electron density acceptor sites [40]. The iodination reaction on the partially fluorinated rings in **9b** was carried out at low temperature (−78°C) by using BuLi/I_2 in dry THF under N_2 atmosphere. Unfortunately the addition in *para* position of the iodine atom occurred partially and a mixture of the starting material **9b** and the iodinated product **2b** was recovered as confirmed by analysis of ^{19}F-NMR spectrum (see Figure S1 in Supplementary Material available online at http://dx.doi.org/10.1155/2015/827592). In the region of −140 ppm the presence of two signals, −140 and −144 ppm,

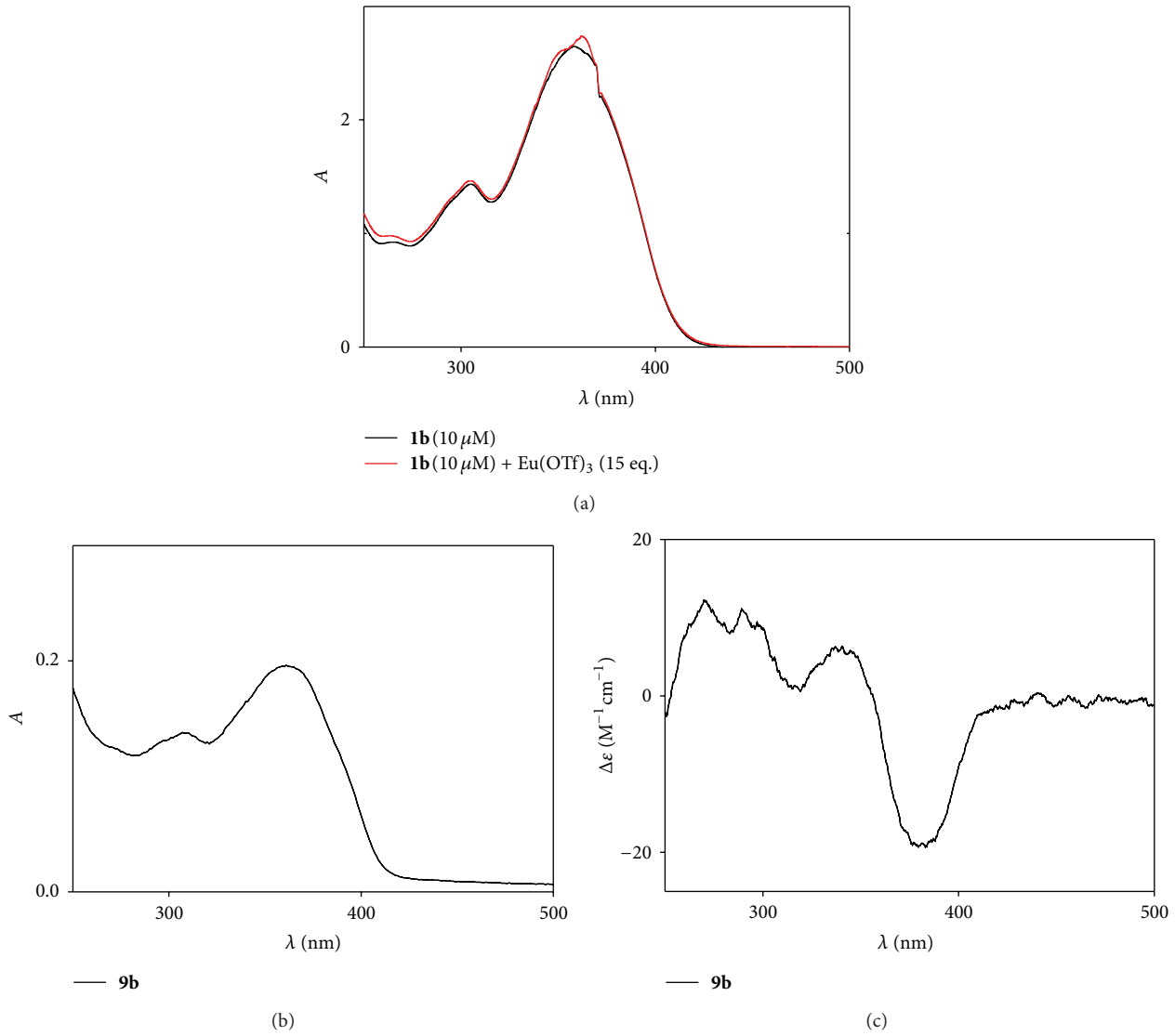


FIGURE 3: (a) Titration experiment of **1b** with $Eu(OTf)_3$ in MeCN. ((b) and (c)) UV and CD spectra of **9b** (1 μM, MeCN).

respectively, confirmed the occurrence of unreacted starting material **9b** while the presence of the peak at −123 ppm, characteristic for fluorine atoms on an aromatic moiety in *ortho* position to an iodine atom, suggested the formation of small amount of iodinated system. Other small peaks at −136 and −121 ppm which were detected in the spectrum highlighted the possible formation of different side products arising from the iodination reaction. The best ratio between hydrogenated and iodinated compound was 10 : 3. Several attempts to purify this mixture have been carried out using standard chromatography, crystallization, and cocrystallization methods; however neither a fully purification nor an enrichment in the mixture of the iodinated compound was obtained. Further attempts have been made to obtain the target halogen bonding donor compound by chaining the experimental conditions, mainly the temperature; however pure iodinated system was never isolated.

2.2. Absorption, Complexation, and Chiroptical Properties. We have recently reported on the characterization of supramolecular complexes involving push-pull chromophores in which the electron-withdrawing molecular fragment is a malonate moiety, and we have demonstrated that this moiety is able to form supramolecular, reversible complexes with metal cations (such as lanthanides) behaving as Lewis Acids [30–35]. The peculiar nature of these complexes is testified by a large red shift (ca. 100 nm) of the intramolecular charge-transfer absorption band (ICT) upon complexation. In order to verify the potential of compound **1b** for complexation and supramolecular polarization, we performed titrations in MeCN using our previously used probes Eu^{3+} and Sc^{3+}, as trifluoromethanesulfonate salts, since they are readily dissolved in MeCN. As shown in Figure 3(a) the addition of up to 15 equivalents of $Eu(OTf)_3$ resulted in negligible changes in the UV/Vis spectra.

Essentially identical results were obtained with $Sc(OTf)_3$. This could be caused by an inefficient complexation of the conjugated malonate moiety in **1b** with the metal center in these conditions. In any case, since the red shift previously observed is completely lacking, the utility of **1** as supramolecularly polarizable dyes is reduced. The UV spectrum of ligand **1b** alone showed the low energy absorption band, attributable to the Intramolecular Charge Transfer band, at 358 nm, which is similar to that obtained for **9b** (361 nm) and to those obtained for pyridine-terminated analogous compounds [39]. The CD spectra of **9b** showed the classical exciton couplet signature typical of binaphthyl systems, centered at 360 nm, coincident, as expected, with the ICT λ_{max} of the compound.

3. Conclusions

We have reported the synthesis and experimental characterization of binaphthyl-based push-pull dyes of novel conception. The synthetic methodologies, building on enantiopure known binaphthyl derivatives, have been demonstrated to be viable for the construction of the π-bridge with the required stereospecificity regarding the newly formed double bond. In the case of dyes **1**, a more thorough study on their inability to give the expected UV/Vis response upon interaction with the metal cation will be carried out in the near future. Regarding dyes **2**, the failure of the final iodination step suggests the possibility of the introduction of a fully functional supramolecular unit from a suitable iodinated phosphonium salt through the Wittig reaction. We are currently developing this synthetic approach.

Appendix

Experimental

General Experimental. All available compounds were purchased from commercial sources and used as received. Compounds **3a** [41], **3b** [39], **5** [42], and **8** [43] were prepared as previously described. THF (Na, benzophenone), Et_2O (Na, benzophenone), and CH_2Cl_2 (CaH_2) were dried and distilled before use. Analytical thin layer chromatography was performed on silica gel, chromophore loaded, commercially available plates. Flash chromatography was carried out using silica gel (pore size 60 Å, 230–400 mesh). ^{1}H and ^{13}C NMR spectra were recorded from solutions in $CDCl_3$ on 200 300 MHz or 500 MHz spectrometer with the solvent residual proton signal or tetramethylsilane as a standard. The UV/Vis spectroscopic studies were recorded using commercially available spectrophotometers. Optical rotations were measured on a polarimeter in a 10 cm cell with a sodium lamp (λ = 589 nm) and are reported as follows: $[\alpha]^{rt}_D$ (c = mg(mL)$^{-1}$, solvent). CD spectra were recorded at 25°C at a scanning speed of 50 nm min^{-1} and were background corrected. Each spectrum is the instrument average of four consecutive scans. Mass spectra were recorded using an electrospray ionization instrument (ESI).

General Procedure for the Titration Experiments. The titration experiments were conducted as follows: to a stock solution of the ligand (solution A) in MeCN (UV/Vis spectroscopic grade), several aliquots of the guest (solution B) were added. Solution B is formed by the lanthanide triflate at higher concentration dissolved in solution A, in order to maintain the ligand always at the same, constant concentration.

*Compound **1b**.* A solution of **3b** (58 mg, 0.101 mmol), dimethyl malonate **4** (43 mg, 0.32 mmol), and three drops of piperidine in benzene (5 mL) was stirred at reflux with a Dean-Stark apparatus for 15 h. The solvent was removed *in vacuo* and the reaction mixture was then treated with H_2O (10 mL) at room temperature, extracted with AcOEt (3 × 20 mL), and dried (Na_2SO_4). The reaction mixture was purified by flash column chromatography (SiO_2; hexane/AcOEt: 1/1 to 3/7) to afford **1b** as a yellow solid (40 mg, 50%). MS(ESI): *m/z* 825 ([M + Na]$^+$, 100%), 1627 ([2M + Na]$^+$, 100%). ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C) δ = 8.29 (s, 2H; -C<u>H</u>=C(COOMe)$_2$), 7.97 (d, 2H; binaphthyl), 7.80 (s, 2H; -binaphthyl), 7.74 (d, 2H; -CH-vinyl, J = 16 Hz), 7.63 (d, 4H; -ArH), 7.5–7.1 (m, 16H; -CH-binaphthyl, -CH-vinyl and ArH), 3.91 (s, 6H; -COOMe), 3.88 (s, 6H; -COOMe), 3.43 (s, 6H; -OC<u>H</u>$_3$). ^{13}C NMR ($CDCl_3$, 75 MHz, 25°C) δ = 167.2 (C=O), 164.5 (C=O), 154.4 (Cq), 142.3 (CH), 140.1 (Cq), 133.8 (Cq), 131.8 (Cq), 130.7 (Cq), 130.5 (Cq), 130.0 (CH), 129.3 (CH), 128.2 (CH), 126.9 (CH), 126.5 (CH), 126.0 (CH), 125.6 (CH), 125.2 (CH), 125.1 (CH), 124.7 (Cq), 61.3 (CH_3), 52.7 (COO<u>C</u>H$_3$), 52.6 (COO<u>C</u>H$_3$).

*Compound **6**.* A solution of **5** (586 mg, 1.87 mmol) and triethyl phosphite (15.7 g, 94.3 mmol, 50 eq) was refluxed in toluene (60 mL) for 24 h. After cooling, the solvent and excess phosphite were removed under vacuo, and the product was purified by column chromatography (hexane/ethyl acetate 1/4 to 1/9), to yield compound **6** as a yellow oil (559 mg, 81%). ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C) δ = 7.75 (s, 1H; Ar-C<u>H</u>=C(COOMe)$_2$), 7.40–7.28 (m, 4H; Ar<u>H</u>), 4.00 (m, 4H; P(O)OC<u>H</u>$_2$CH$_3$), 3.85 (s, 6H; -COOC<u>H</u>$_3$), 3.17 (d, 2H; ArC<u>H</u>$_2$P(O)OEt), 1.27 (t, 6H; P(O)OCH$_2$C<u>H</u>$_3$). ^{13}CNMR ($CDCl_3$, 75 MHz, 25°C) δ = 167.1, 164.4, 142.3, 134.7, 131.2, 130.2, 129.5, 125.1, 62.1, 52.6, 34.6, 32.8, 16.3.

*Compound **7**.* A solution of PPh_3 (295 mg, 1.13 mmol) and **5** (344 mg, 1.10 mmol) was refluxed in toluene (3 mL) for 6 h. After cooling, the precipitate was filtered off to yield compound **7** as an orange solid (310 mg, 49%). ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C) δ = 7.82–7.60 (m, 16H; Ar<u>H</u>), 7.22–7.13 (m, 4H; Ar<u>H</u>), 5.66 (d, 2H; ArC<u>H</u>$_2$PPh$_3$), 3.85 (s, 3H; -COOC<u>H</u>$_3$), 3.83 (s, 3H; -COOC<u>H</u>$_3$). ^{13}C NMR ($CDCl_3$, 75 MHz, 25°C) δ = 166.8, 164.2, 141.7, 134.9, 134.4, 132.5, 132.1, 130.3, 130.1, 130.0, 129.4, 126.0, 118.1, 117.0, 52.7, 30.7, 30.1.

*Compound **9a**.* NaH (5 mg, 0.2 mmol) was added to a solution of the phosphonium salt **8** (80 mg, 0.16 mmol) in dry DMF (2 mL). After stirring for 30 min at room temperature, a solution of compound **3a** (27 mg, 0.07 mmol) in dry DMF (1 mL) was added. After stirring at 40°C for 15 h, H_2O was added and the mixture was extracted with CH_2Cl_2. The

organic phase was dried (Na_2SO_4) and the reaction mixture purified by flash chromatography (SiO_2; hexane/CH_2Cl_2 7/3) to yield **9a** as a white solid (10 mg, 20%). MS(ESI): *m/z* 663 ($[M + H]^+$, 100%), 685 ($[M + Na]^+$, 97%), 1347 ($[2M + Na]^+$, 40%). ^{1}H NMR ($CDCl_3$, 200 MHz, 25°C) δ = 8.30 (s, 2H; binaphthyl), 8.03 (d, 2H; -CH-vinyl, J = 16 Hz), 8.01 (d, 2H; binaphthyl), 7.49–7.16 (m, 10H; binaphthyl and -CH-vinyl), 6.96 (m, 2H; -CH- tetrafluorophenyl), 3.45 (s, 6H; -OCH_3).

Compound ***9b***. NaH (45 mg, 1.76 mmol) was added to a solution of the phosphonium salt **8** (593 mg, 1.17 mmol) in dry DMF (2 mL). After stirring for 30 min at room temperature, a solution of compound **3b** (337 mg, 0.59 mmol) in dry DMF (3 mL) was added. After stirring at 40°C for 15 h, H_2O was added and the mixture was extracted with Et_2O. The organic phase was dried (Na_2SO_4) and the reaction mixture purified by flash chromatography (SiO_2; hexane/CH_2Cl_2 7/3) to yield **9b** as a yellow solid (350 mg, 69%). $[\alpha]^{25}_D$ = −505.6° (c = 0.0016, CH_2Cl_2). MS(ESI): *m/z* 866 ($[M + H]^+$, 100%). ^{1}H NMR ($CDCl_3$, 300 MHz, 25°C) δ = 8.30 (s, 2H; binaphthyl), 7.96 (d, 2H; binaphthyl), 7.71–7.57 (m, 10H; -ArH- and -CH-vinyl), 7.51–7.41 (m, 6H; binaphthyl and -CH-vinyl), 7.26–7.10 (m, 6H; binaphthyl and -CH-vinyl), 6.96 (m, 2H; -CH-tetrafluorophenyl), 3.45 (s, 6H; -OCH_3). ^{13}C NMR ($CDCl_3$, 75 MHz, 25°C) δ = 154.4 (Cq), 147.0 (CF), 144.0 (CF), 138.3 (Cq), 136.9 (Cq), 135.9 (Cq), 133.7 (Cq), 130.8 (Cq), 129.8 (CH), 128.1 (CH), 127.3 (2CH), 127.0 (2CH), 126.3 (CH), 126.2 (CH), 125.6 (CH), 125.1 (CH), 124.6 (CH), 113.6 (CH), 113.0 (Cq), 104.0 (CH), 103.6 (CH), 61.3 (CH_3).

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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